

Formation of self-assembled micro- and nano-domain structures in uniaxial ferroelectrics

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Abstract. We present the experimental study of appearance of domain wall shape instabilities and self-assembled domain structures in uniaxial ferroelectrics lithium niobate and lithium tantalate covered by artificial dielectric layer. The domain structure evolution has been considered as a manifestation of nucleation processes similar to the first order phase transformation. The necessary conditions for formation of self-assembled domain structures including the highly non-equilibrium switching conditions and stability of concave angles were proposed. The formation of the self-assembled domain shape instabilities under application of the uniform external electric field during switching (domain growth) and backswitching (domain shrinkage) has been studied experimentally with these conditions fulfilled. The formation of the bumps at the vortexes of hexagon domain for diameter above 3 - 5 μm with subsequent oriented growth was obtained in stoichiometric lithium tantalate. The formation of quasi-regular fish-bone domain structure has been revealed during spontaneous backswitching in Mg doped lithium niobate. The resulted structure consisted of the narrow residual domains with width from 200 to 500 nm appeared as a result of finger growth to the center of hexagon domain. The obtained decreasing of the number of the residual domains during growth has been attributed to strong electrostatic interaction of domain walls.

1. Introduction

The study of kinetics of first order phase transitions in highly non-equilibrium conditions became extremely urgent [1]. The formation of self-assembled structures including the dendrite ones was demonstrated experimentally [2] and the phase diagram of the most common structure types was predicted [3–5]. However the first order phase transitions including the crystallization from the melt poses the limited range of control parameters thus prohibiting the realization of all predicted types of structure in one system. This fact stimulates searching of new systems with simple variation of control parameters, *in situ* and high resolution structure visualization. It is known that the evolution of ferroelectric domains during polarization reversal can be considered as an analogy of the first-order phase transformation with electric field as a driving force [6,7]. The highly non-equilibrium switching conditions can be realized in ferroelectrics in wide range of control parameters. The complementary methods of domain visualization with high spatial and temporal resolutions are available [8,9].

The single crystalline lithium niobate (LiNbO_3 , LN) and lithium tantalate (LiTaO_3 , LT) represent the most investigated ferroelectric materials. Their great practical importance enabled the growth of the large crystals with extremely high uniformity [8]. The static domain structure can be visualized by scanning probe microscopy and scanning electron microscopy with resolution down to 2 nm and by Raman confocal microscopy in the bulk with resolution about 300 nm. Thus the single crystals of LN



and LT are perfect model materials for investigation of self-assembling in highly non-equilibrium switching conditions.

In this paper we review the experimental studies of appearance and growth of domain wall shape instabilities and self-assembled domain structures in uniaxial ferroelectric LN and LT crystals (C_{3v} symmetry) covered by uniform artificial surface dielectric layer.

2. Experiment

The samples represented the 1-mm-thick plates polished to optical grade. The artificial dielectric layer represented the 3- μ m-thick photoresist deposited on Z+ polar surface of the samples. The uniform liquid electrodes were used for field application. The single rectangular electric field pulse was applied using the high-voltage amplifier. The domain structure after partial polarization reversal was revealed by shallow selective chemical etching and the relief was visualized using the optical microscope (Olympus BX51, Japan) and scanning probe microscope.

3. The model of formation of dendrite structures in uniaxial ferroelectrics

The domain structure evolution has been considered as a manifestation of various nucleation processes similar to the first order phase transition [10,11]. Within this kinetic approach the neighboring domains are similar to the volumes of different phases divided by interfaces (domain walls). The domain growth is a result of thermally activated generation of one-, two-, and three-dimensional nuclei (1D-, 2D-, and 3D-nucleation) with preferred orientation of the spontaneous polarization. The shape of growing isolated domain is defined by position of the nucleation sites at the domain walls. The usual hexagon domain shape in LN obtained in slow (equilibrium) switching conditions is caused by determined nucleation at three non-adjacent hexagon vertexes and kink propagation in three Y directions [7]. In equilibrium switching conditions with effective screening the domain shape stability effect is observed which represents the rapid recover of hexagon shape after domain merging [12].

The nucleation probability is governed by local value of the electric field averaged over the nucleus size ("local field" E_{loc}) [6,7]. It is clear that E_{loc} is spatially inhomogeneous and changes essentially during polarization reversal. E_{loc} includes: (1) the external field (E_{ex}) produced by applied voltage, (2) the residual depolarization field (E_{rd}) produced by bound charges and external screening charges, which depends on the domain structure, (3) the bulk screening field (E_b) governed by bulk screening processes [13,14].

$$E_{loc}(r,t) = E_{ex}(r) + E_{rd}(r,t) + E_b(r,t) \quad (1)$$

The three types of the bulk screening mechanisms have been considered: (1) redistribution of the bulk charges [6,15], (2) reorientation of the defect dipoles [15], (3) injection of the carriers from the electrode through the dielectric gap [16,17]. All bulk screening mechanisms are comparatively slow with time constants ranged from milliseconds to days and months. The retardation of bulk screening results in non-equilibrium switching conditions and qualitative change of the domain structure evolution.

The self-assembled formation of complicated domain shapes is possible only under highly non-equilibrium switching conditions (ineffective screening) and stable concave angles which allows preserving the appeared complex domain shapes.

The ineffective external screening can be realized by the artificial surface dielectric layer [7,18], switching without electrodes by pyroelectric field [19] or spontaneous backswitching after external field switch off by break of external circuit [20]. The stability of the concave angles is obtained for isotropic domain growth due to ionic conductivity which dominated in LN and LT crystals at elevated temperatures (above 150°C), and hampering of domain merging due to electrostatic interaction of the approaching domain walls.

In this paper we have analyzed the formation of the self-assembled domain shape instability under application of the uniform external electric field during switching (domain growth) and backswitching (domain shrinkage).

4. Experimental results

The domain wall shape instability was studied in stoichiometric LT crystal during the domain growth in the field 2 kV/mm. The process starts from growth of hexagon domain. The formation of six bumps at the domain vortices was obtained for domain diameter above 3 - 5 μm (Fig. 1a). The formed bumps grow mostly in Y directions without merging (Fig. 1a, b).

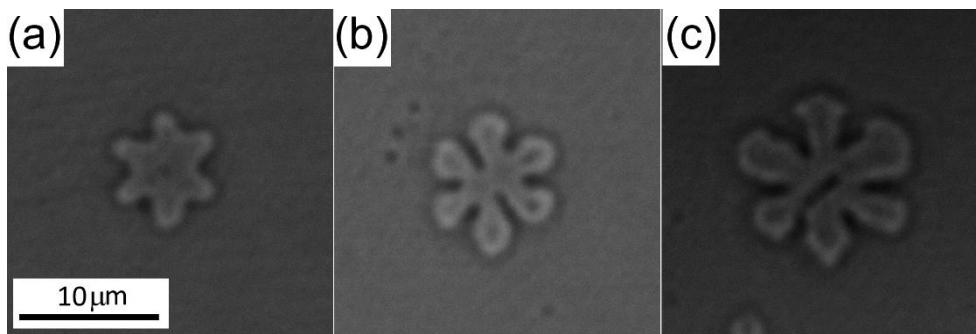


Figure 1. The stages of domain wall shape instability formation. Optical microscopy, transmitted light, phase contrast.

The domain shrinkage was studied in the MgO doped LN crystal. The experiment started by the application of short rectangular pulse of external electric field leading to growth of hexagonal domain. The back switching after external field abrupt switched off with break of external circuit leads to formation of quasi-regular fish-bone structure. The resulting structure consists of residual domains appeared as result of oriented growth of stripe domains (“fingers”) from the boundary of hexagon domain to the center (Fig. 2a). The period of stripes is about one micron and the width of residual domains ranged from 200 to 500 nm (Fig. 2b). The nucleation of the short branches is obtained. The obtained increasing of the domain period (decreasing of the number of the fingers) during finger growth to the center can be attributed to strong electrostatic interactions of the neighbouring domain walls.

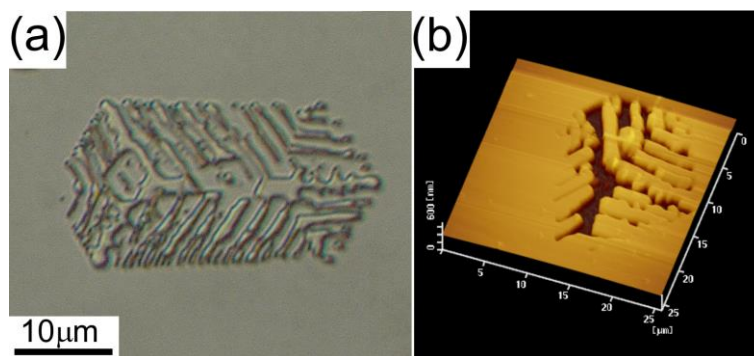


Figure 2. The fish-bone domain structures obtained as a result of spontaneous backswitching in MgO doped LN single crystals, visualized by: (a) optical microscopy, (b) scanning probe microscopy.

5. References

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